

PATENT SPECIFICATION

(11) 1 415 853

(21) Application No. 6642/72 (22) Filed 12 Feb. 1972

(23) Complete Specification filed 5 Feb. 1973

(44) Complete Specification published 26 Nov. 1975

(51) INT CL² B05D 7/00; F16D 69/02

(52) Index at acceptance

B2E 203 20Y 368 413 41X 41Y 498 570 648

C4X 4

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(54) ANTI-OXIDATION COATINGS

(71) We, DUNLOP LIMITED, a British Company of Dunlop House, Ryder Street, St. James's, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of treating a pre-formed carbon or graphite friction element to protect a surface thereof against oxidation, and is especially though not exclusively, concerned with the protection of exposed non-wearing surfaces of carbon or graphite friction element for brakes.

Carbon and graphite materials oxidise rapidly on exposure to air at temperatures in excess of 500°C., thus when such materials are used as friction elements for brakes a considerable problem can arise. The problem is particularly acute in aircraft disc brakes where the operating temperature is often in excess of 500°C. A small weight loss (in the order of 10%) due to oxidation of a carbon or graphite friction element is sufficient severely to impair the mechanical efficiency of the brake.

Methods conventionally used to decrease oxidation rates involve coating the carbon with such materials as flame-sprayed metals or glassy coatings, or by impregnation of the carbon with chemicals such as phosphates. The coatings are difficult to apply and not particularly effective, while the impregnated chemicals can adversely affect certain properties of the materials.

It is an object of this invention to provide an improved method for preventing oxidation of carbon or graphite friction elements.

It is also an object of this invention to provide friction elements of carbon and/or graphite with a coating which prevents oxidation of the carbon.

According to the present invention there is provided a method of treating a pre-formed carbon or graphite friction element to protect a surface thereof against oxidation, comprising coating said surface with a mixture of

at least one boron-containing material and a carbonisable organic material and carbonising the organic material at an elevated temperature to form a binder which will hold the boron-containing material in position on said surface.

The organic material may be a carbonisable organic liquid or a carbonisable solid in a liquid medium, for example, as a solution, suspension or dispersion, such that the material can be carbonised to give a carbonaceous coating which holds the boron compound in place. A suitable organic compound for the binder may be a phenol formaldehyde type of resin which can itself be liquid or in solution in, for example, acetone or alcohol. Other binder materials include urea-formaldehyde resins, coal tar (pitch), and certain hydrocarbons.

The boron-containing materials may include boron, boron oxides, boron carbide and various borides of chromium, zirconium, tantalum and tungsten.

The carbonising of the binder may be carried out by a heat treatment process or the elevated temperature which occurs in use of the carbon friction element can be relied on to carbonise the binder.

Various embodiments of the invention will now be described, by way of example.

A method of protecting the non-wearing surfaces of an annular carbon or graphite friction element for an aircraft multi-disc brake comprises coating those areas of the friction element (the substrate) which are liable to oxidation during braking with a mixture of at least one boron-containing material and a carbonisable organic material and carbonising the organic material at an elevated temperature to form a binder which holds the boron compound in place.

Boron and various boron compounds may be used in conjunction with the organic material (the binder) to prevent or substantially to reduce oxidation of the carbon in the friction element. The following borides are some of many considered satisfactory:—

- a) the borides of chromium
- b) zirconium diboride

- c) tantalum monoboride
 d) titanium diboride
 e) tungsten diboride
 f) ditungsten monoboride
- 5 Also mixed oxides such as aluminium with boron $9\text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3$ may be used.
- The choice of binder is similarly wide, since the purpose of the binder is merely to char to carbon and to provide an effectively bonded surface coating. Therefore the binder should be applied as a carbonisable organic liquid or as a solution, suspension or dispersion of a carbonisable solid in a liquid with the restriction that the compounds have a carbon yield on charring of 20% or greater. Suitable materials for this purpose include phenol-based resins such as phenol formaldehyde resins or urea formaldehyde resins or generally most cross-linked resins which can be liquid or in solution in acetone or alcohol.
- 10 Certain hydrocarbons such as sugar solution and coal tar may also be satisfactorily employed as the binding agent.
- 15 In one example, the non-wearing surfaces of a friction element are painted with the following mixture:—
- a) 100 parts by weight of acetone (solvent)
 b) 25 parts by weight of phenol formaldehyde resin No. VW 65059 manufactured by BXL (Bakelite Xylonite Ltd.)
 c) 25 parts by weight of — 300 mesh boron powder (British standard sieve size).
- 20 The resin coating is then cured by heating to a temperature of 150—200°C. in air. The curing process is carried out to firstly drive off the solvent, in this case acetone, and secondly to allow the cross-linking of the phenol formaldehyde resin. After completion of the curing process the friction element is placed in a firing oven in an inert atmosphere in this case nitrogen. The friction element is subsequently heated to a temperature of at least 800°C. causing carbonisation of the binder (the resin) leaving the non-wearing surfaces of the friction element with a permeable carbon coating containing discrete particles of boron which provide excellent protection against the oxidation of the friction element.
- 25 If in a further example the whole of the friction element is coated with the mixture, firing can quite satisfactorily be carried out in an atmosphere of air since there are no exposed carbon surfaces.
- As an alternative to carbonising the resin on a friction element in an oven at 800°C., the coated friction element once the resin has been cured may be assembled into its respective brake. The use of the brake at temperatures reaching over 500°C. is sufficient to carbonise the binder and produce a permeable anti-oxidation coating on the non-wearing surfaces of the friction element.
- 30 The following results (Tables 1 and 2) were obtained from oxidation tests carried out on $\frac{1}{2}$ inch cubes of a graphite fibre reinforced carbon heated at 500°C. in static air. Test results are also included from identically sized specimens which had previously been coated with various anti-oxidation mixtures, the resin cured at 300°C. and fired at 800°C. in air. Test results on an un-coated commercial graphite (ATJ ex. Acheson Co. Ltd.) at 600°C. are also included.
- 35 Tables 3 and 4 include oxidation test results carried out on both coated and uncoated 1 centimetre cubes in static air at 500°C. and 820°C.

TABLE I

Oxidation tests

Tests at 500°C.

Percentage weight loss

Time in hours as shown.	1 hour	10 hours	25 hours	50 hours	100 hours
<u>Specimen No.</u>					
1	7.81	31.44	54.85	66.36	84.9
2	0.98	1.96	3.22	5.28	13.02
3	0.78	1.80	2.51	4.03	12.56
4	0.79	1.99	3.34	5.46	15.84

Time in hours as shown	1 hour	10 hours	29 hours
<u>Specimen No.</u>			
5	2.35	26.1	76.5
6	0.66	1.69	8.38
7	0.60	2.04	5.78

TABLE II

Specimen Treatment

Specimen No.	Treatment
1	Untreated standard reinforced carbon
2	Zirconium diboride and phenolic resin in acetone on reinforced carbon.
3	Zirconium diboride and phenolic resin in furfuryl alcohol on reinforced carbon.
4	Boron carbide and phenolic resin in acetone on reinforced carbon.
5	Untreated standard ATJ (ex Acheson Co. Ltd.)
6	Chromium diboride + phenolic resin in acetone on ATJ.
7	Zirconium diboride + phenolic resin in acetone on ATJ.

TABLE III

Oxidation tests on 1 cm cubes in static air at 550°C.

Time in hours as shown.	Percentage weight loss		
	4 hours	10 hours	50 hours
Carbon material standard uncoated	17.5	32	65
Carbon material having carbonised resin coating	12	19	65
Carbon material having coating of boron carbide + carbonised resin	1	2	6
Carbon material having coating of chromium diboride + carbonised resin	1	2	5

TABLE IV

Oxidation tests on 1 cm cubes in static air at 820°C.

Time in hours as shown	Percentage weight loss		
	1 hour	4 hours	9 hours
Carbon material, standard uncoated	19	73	100
Carbon material having coating of boron carbide + carbonised resin	None detected	None detected	1

5 The above test results conclusively show
the drastic reduction in percentage weight loss
due to oxidation of specimens when coated
with various mixtures comprising boron com-
pounds and carbonised binder resins. The per-
centage weight loss in the coated articles is
sufficiently low to allow carbon friction mat-
10 erials to be used in aircraft brakes without
fear of breakdown due to oxidation.

WHAT WE CLAIM IS:—

15 1. A method of treating a pre-formed car-
bon or graphite friction element to protect a
surface thereof against oxidation, comprising
coating said surface with a mixture of at least
one boron-containing material and a carbon-
isable organic material and carbonising the
organic material at an elevated temperature to
20 form a binder which will hold the boron-con-

taining material in position on said surface.

2. A method as claimed in claim 1 in which
the mixture is a mixture of discrete particles
of at least one boron-containing material and a
carbonisable organic liquid or a carbonisable
organic solid in a liquid medium. 25

3. A method as claimed in claim 2 in which
the mixture consists of discrete particles of at
least one boron-containing material and a car-
bonisable resin which mixture is painted onto
the said surface, and wherein the resin is cured
and subsequently the friction element is heated
to a temperature sufficient to carbonise the
resin. 30

4. A method as claimed in any one of
claims 1—3 wherein the binder is an organic
compound having a carbon yield on charring
of greater than 20%. 35

5. A method as claimed in claim 4 wherein

- said surface is coated with a mixture in which the binder is one of the following cross-linked resins:—
- 5 a) Phenol formaldehyde resin
 - b) Urea formaldehyde
6. A method as claimed in any one of the preceding claims wherein the boron-containing material used is selected from the group consisting of boron, a boron oxide, a boron carbide or a boride of chromium, zirconium, tantalum, titanium or tungsten.
- 10 7. A method as claimed in any one of the preceding claims wherein the mixture is carbonised in air.
8. A method as claimed in any one of claims 1—6 wherein the mixture is carbonised in an inert atmosphere. 15
9. A method of treating a pre-formed carbon or graphite friction element to protect a surface thereof against oxidation substantially as hereinbefore described. 20
10. A carbon or graphite friction element treated to protect a surface thereof against oxidation by the method claimed in any one of the preceding claims. 25

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1975.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.